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Stress Corrosion Cracking of Titanium Alloys: Brief Summary of Electrochemical Mechanisms

T. R. Beck

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Stress Corrosion Cracking of Titanium Alloys:
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1.0 SUMMARY

As this report marks the end of two years' work under this contract on stress corrosion cracking of titanium alloys, a brief summary of the electrochemical mechanisms as now understood is presented. A pictorial presentation is given for the currently envisaged electrochemical events in a propagating stress corrosion crack in titanium based on SCC experiments, electrochemical kinetics data on newly generated metal surface and quantitative mass-transport-kinetics model formulation. A halide ion interaction at the tip of the crack is indicated as involved in the SCC mechanism. Some approximate limiting cases from the more general mass-transport-kinetic formulation are presented and compared to experimental SCC data.

2.0 INTRODUCTION

This report describes part of a study of stress corrosion cracking of titanium alloys initiated in July, 1965^[1] and continued under NASA sponsorship beginning July, 1966^[2]. This is the eighth Quarterly Report in the series (3, 4, 5, 6, 7, 8, 9) and covers the period April 1 through June 30, 1968.

Work was accomplished in two areas in this past quarter: a study of steady-state crack propagation with an aluminum : 2.5% Mg - 6% Zn alloy under potentiostatic conditions in chloride solutions, and a reexamination of kinetics of oxidation of freshly generated titanium metal surfaces. Work in each of these areas is in an early stage and will be only briefly mentioned here and described in more detail in the next quarterly report.

The study of SCC of aluminum alloys is in collaboration with Dr. M. O. Speidel using the techniques previously developed for studies with titanium alloys. Similar trends were found in respect to an increase in velocity with potential up to the pitting potential and then a decrease with potential, although the velocities were about two orders of magnitude lower than for titanium and the cracks were intercrystalline rather than transcrystalline.

Reexamination of kinetics of oxidation of freshly generated titanium surfaces was for the purpose of determining if an appreciable amount of soluble titanium species is formed in parallel with formation of oxide as predicted by the mass-transport-kinetic model for SCC of titanium (9). A rotating ring-disc electrode was built with a titanium

disc and gold ring for this determination. The titanium disc is scraped with a sapphire cutter under potentiostatic conditions and soluble Ti^{+3} species determined by oxidation to Ti^{+4} at the ring.

Preliminary experiments indicate that a large fraction of the current to the disc can be accounted for by formation of Ti^{+3} .

In that this report marks the completion of two years' work on the stress corrosion cracking of titanium it appeared appropriate to summarize the findings on the electrochemical mechanisms in a concise form. The paper presented at the International Conference on Titanium - London, May 21-24, 1968 on this subject is therefore reproduced here.

3.0 TECHNICAL DISCUSSION

After the recent discovery (10) of stress corrosion cracking (SCC) susceptibility of certain titanium alloys in sea water, speculation began concerning the mechanism. The commonly proposed SCC mechanisms (11) of hydrogen embrittlement, oxide wedging or stepwise formation and fracture, anodic dissolution at the crack tip and adsorption of active species were considered. Because each of these mechanisms should be sensitive to potential, but in different ways, a series of SCC experiments was conducted in which specimens of a susceptible Ti-8% Al-1% Mo-1% alloy were fractured in various salt solutions at various fixed potentials.

It was found that SCC of this alloy occurred only in the presence of three ions in aqueous solutions - chloride, bromide and iodide (12). The specimens were cathodically protected at negative potentials but the strength decreased significantly at potentials more positive than -1 volt to the saturated calomel electrode (SCE). Moreover, velocity of crack propagation and the current flowing into the propagating cracks were linearly related to potential. Clearly there appeared to be an electrochemical step involved in SCC of titanium.

Electrochemical kinetics data were also obtained for formation of oxide and hydrogen ion reduction on fresh surfaces generated by fast fracture (13). These data together with the equations for ionic mass transport, relation of ionic flux and current, electroneutrality and mass balance provided a basis for a model quantitatively describing the electrochemical events in a propagating SCC crack. The model has

been described in detail elsewhere (14) so the results shall only be summarized here and a few important limiting cases of the more general formulation given.

A pictorial summary of the currently envisaged electrochemical events in a propagating stress corrosion crack is shown in Fig. 1. In the model a steady-state mass-transport condition is assumed in a stagnant wedge-shaped body of electrolyte which the walls slip past at the crack propagation velocity, V . A current of halide ions corresponding approximately to formation of a monolayer flows into the "tip zone" where these ions are apparently instrumental in the cleavage process either through chemical or surface processes. In the "monolayer zone" the halide is displaced from the walls by a monolayer of oxide and recycles to the tip. Some simultaneous hydrogen ion reduction occurs at the negative potential of the "monolayer zone". the small amount of hydrogen presumably entering the metal. The hydrogen ion reduction current density decreases at the more positive potential of the "multilayer zone" where formation of oxide and soluble titanium species occur in parallel. The current is carried out of the crack by titanium ions and hydrogen ions produced by oxide formation. The generation of hydrogen ions in the crack causes the solution to become acid in respect to the bulk solution outside the crack.

EVIDENCE FOR HALIDE INTERACTION AT CRACK TIP

There is no direct experimental proof that halide ions are the SCC agents at the crack tip in aqueous solutions at this time because

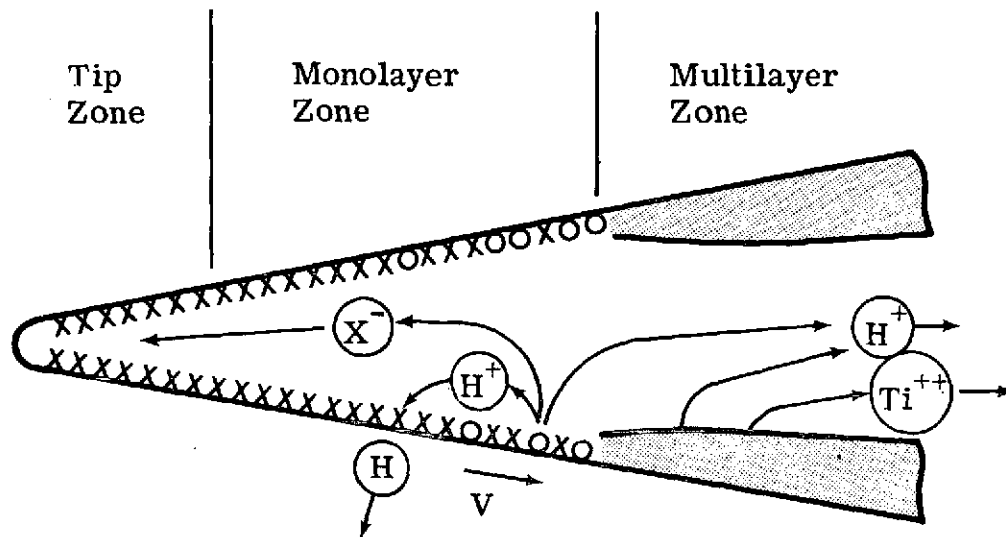


Figure 1. Pictorial Presentation of Currently Envisaged Electrochemical Events in a Propagating Stress Corrosion Crack in Titanium (not to scale)
 X represents adsorbed halide
 O represents monolayer of oxide

it has not been possible to see or sample the events of a molecular scale near the crack tip. There is now, however, a large body of evidence supporting the concept. There are also a number of bases for rejecting oxide or hydride mechanisms as being directly responsible for SCC of titanium in aqueous solutions. Some of the supporting evidence for a halide mechanism will be summarized here.

The specificity of chloride, bromide, and iodide ions as SCC agents is a strong clue that they are involved in the critical process. Other anions, such as fluoride, hydroxide, sulfate, nitrate, sulfide, cyanide and thiocyanate are not SCC agents and in fact act as inhibitors when present in sufficient excess in respect to chloride, bromide and iodide. If oxide or hydride were involved as primary SCC mechanisms at the tip, this specificity to chloride, bromide and iodide ions would not be expected.

Various organic halogen compounds are also good SCC agents (15), including -- carbon tetrachloride, chloroform, methylene chloride, methylene bromide and trichlorethylene. Carbon tetrachloride, which contains no hydrogen in the molecule, was the most effective of these organic SCC agents. Addition of benzene, a hydrocarbon, to carbon tetrachloride, tended to inhibit SCC. The fractography from SCC in carbon tetrachloride was indistinguishable from the fractography produced from SCC in aqueous halide solutions. Oxide and hydride SCC mechanisms are not too probable in dry carbon tetrachloride.

There are many similarities between SCC and pitting corrosion of titanium which suggest a very similar mechanism; and pitting certainly involves direct interaction of titanium with halide ions. The same

three anions are the specific pitting agents, and a similar relationship exists of SCC velocity and pitting velocity to potential and to halide ion concentration.

The most important result to come out of the electrochemical mass-transport-kinetic model was that there appeared to be a mass-transport limited current of halide ions going to the crack tip. The magnitude of this current corresponded approximately to the formation of a monolayer of halide ions or of titanium dihalide in the tip zone. Titanium of valence 2 is the thermodynamically stable species of the suspected negative potential of the tip. The activation energy of SCC velocity turned out to be 3.5 Kcal, consistent with a mass-transport limited current of halide ions.

A limiting case for the relation of SCC velocity to halide ion concentration in the bulk solution at the mouth of a crack is

$$V = \frac{z_- F D_- \gamma C_-^0}{2 Q_x \ell \ln (\ell / \delta p)} \quad (1)$$

where: V = SCC velocity in cm/sec, z_- = valence of halide ion, F = 96,500 coulomb/equiv., D_- = diffusivity of halide ion in cm^2/sec , γ = crack opening angle in radians, C_-^0 = bulk concentration of halide ion in mole/ cm^3 , Q_x = charge density of a monolayer of titanium dihalide in coulomb/ cm^2 , ℓ = length of crack from geometric apex to position where there is appreciable flow of solution and current into the crack from the sides (about 1/10 the specimen thickness) in cm, and δp = distance in cm from apex to position in the crack where the width approaches molecular dimensions and the continuum mass-transport

equation becomes in applicable. It was found that experimental SCC velocities approach values predicted by equation 1 at high halide ion concentrations as shown in Fig. 2.

The large departure at low concentration as shown in Fig. 2 has been attributed to recycling of halide ions near the tip caused by displacement of halide by oxide in the monolayer zone. In distilled water, chloride sufficient for SCC is presumably gathered from the residual process chloride remaining in the metal at a parts per million level. Unfortunately, we have had insufficiently precise chloride analyses of the metal to directly test this hypothesis as yet. There is, however, a degree of indirect verification. About a hundred parts per million of sulfate or nitrate added to distilled water is sufficient to completely inhibit SCC (15). The sulfate and nitrate in excess of the chloride concentration gathered from the metal apparently inhibit SCC as they do in more concentrated solutions.

There is an interesting parallel between SCC in water and in methanol which leads to the supposition that essentially the same mechanisms are involved. The velocity of SCC in relatively concentrated solutions of chloride in methanol under potentiostatic conditions is the same within experimental error as in aqueous chloride solutions. This would be expected from a mass-transport limited velocity because the diffusivity of chloride ion is not greatly different in methanol and water. On the other hand, in pure methanol the velocity is on the order of 10^{-4} cm/sec or about an order of magnitude less than in distilled water. If the halide displacement mechanism is operative in these pure solvents, then the velocity in methanol might be expected to be slower

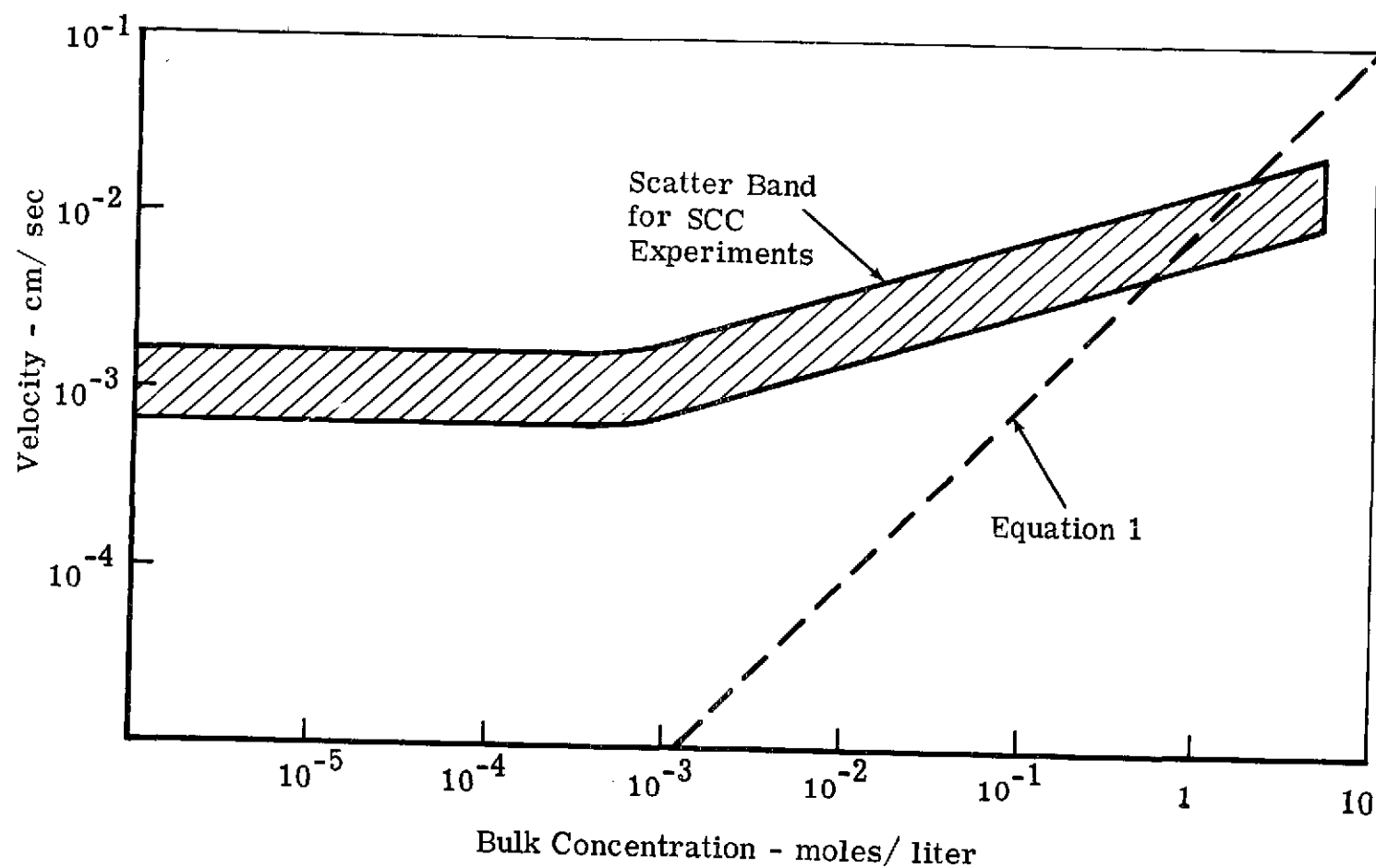


Fig. 2 Relation of SCC Propagation Velocity to Bulk Concentration of Halide Ion and Comparison to Equation 1. (Values of Parameters in Equation 1: $z_- = 1$, $D = 1 \times 10^{-5}$ cm²/sec, $\gamma = 0.05$ radians, $Q_X = 4.2 \times 10^{-4}$ coulomb/cm², $\ell = 10^{-2}$ cm, $\delta p = 10^{-5}$ cm)

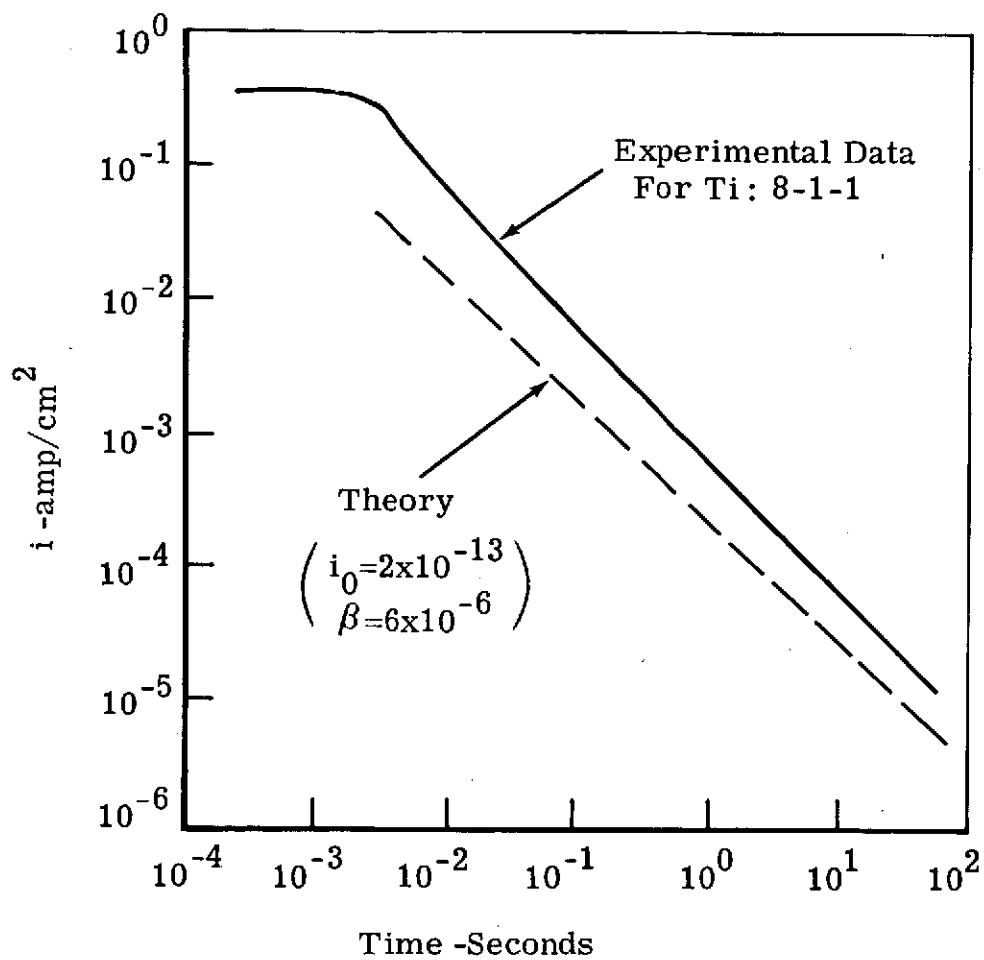


Fig. 3 Kinetic Data for Multilayer Oxide Growth on Ti:8-1-1 Alloy in 0.6M KCl Solution at Zero Volts (SCE)

because methanol is not as good an oxidizing agent as water and the chloride displacement would occur further from the tip. This would result in a lower concentration gradient near the tip and thus a lower mass-transport limited velocity. In further support of the mechanism, only about ten parts per million of sulfate or nitrate are required for inhibition of SCC in methanol (with the lower velocity) in contrast to about 100 ppm in distilled water.

EVIDENCE FOR TiO_2 AND SOLUBLE TITANIUM IONS

Kinetics of oxidation of newly generated Ti:8-1-1 surface was studied by rapidly fracturing metal specimens under potentiostatic conditions in salt solutions and observing change of current with time. Rapid shear fracture of notched SCC specimens was obtained by using a much higher crosshead velocity than used in the SCC tests. A typical plot of current density versus time is given in Fig. 3. The dashed line is for integration of the high-field conduction equation for an oxide film (13) using constants determined for titanium oxide film by Johanson, et al., (16). There appeared to be a reasonable correlation between the theory and experiment. That the experimental current density was higher than predicted by the theory was attributed at the time to higher defect concentration in the oxide from the alloy.

A basic premise to the model formulation for the electrochemistry in a stress corrosion crack was that the kinetic data obtained on the plane fracture surfaces were applicable to the walls of a stress corrosion crack. The model has been described in detail elsewhere but a limiting case for the current entering a crack is presented here. By using the

approximation that $i = k/\tau$ for growth of the oxide film in place of the more complex expression from the high field equation, the current density on the two walls can be integrated to give

$$I^0 = 2V [Q_0 + k \ln (\ell/\delta)] \quad (2)$$

where I^0 = current entering crack in amp/cm, V = crack propagation velocity in cm/sec, Q_0 = charge density of monolayer of oxide in coulomb/cm², k = empirical constant for growth of oxide film in coulomb/cm², δ = distance from apex where monolayer is completed in cm, i = current density for growth of oxide film in amp/cm² and τ = time from start of film growth in sec.

Equation 2 can be compared to experimental SCC data as follows. Assuming $Q_0 = 4.2 \times 10^{-4}$ coulomb/cm² (for a monolayer of oxide ions), $k = 9.0 \times 10^{-4}$ coulomb/cm² (from Fig. 3), $\ell = 10^{-2}$ cm (for a 0.1 cm thick specimen) and $\delta = 10^{-4}$ cm (for 10^{-2} sec to complete first monolayer in Fig. 3 and a velocity on the order of 10^{-2} cm/sec in Fig. 4) gives $I^0 = 9.2 \times 10^{-3}$ V. From the typical experimentally observed relationship of SCC velocity and current flowing into a crack versus applied potential shown in Fig. 4 it can be seen that $I_{exp}^0 \approx 28 \times 10^{-3}$ V. Thus there is an order of magnitude agreement between the current calculated from the kinetic data and the experimentally observed SCC current. Further, the experimental current is larger, consistent with a larger area from observed branching of the crack.

An approximation can also be made for the resistance of the

electrolyte in a wedge shaped crack. It can be seen from Fig. 3 that the oxidation current decreases very rapidly with time. Translated to a crack, the approximation can be made that all of the current flows into a crack to a position of the order of magnitude of δ from the apex. Assuming constant resistivity electrolyte, the resistance of the electrolyte in the crack can be approximated by

$$R = \frac{\rho}{\gamma} \ln(l/\delta) \quad (3)$$

where R = resistance of electrolyte in a unit thickness specimen in ohm cm and ρ = electrolyte resistivity in ohm cm. By using the resistivity of the bulk 0.6M KCl electrolyte (~ 15 ohm cm) and an observed 3-degree crack opening ($\gamma = 0.05$ radians) and the above values of l and δ , $R = 1400$ ohm cm from Equation 3. From the slope of the experimental SCC current versus potential curve in Fig. 4 a resistance of $R_{\text{exp}} = 1700$ ohm cm is determined, constituting a degree of verification of Equation 3.

The more general mass-transport-kinetic model (14), however, shows that this is an oversimplification. The electrolyte in the crack becomes very acid from the hydrogen ion generated by oxidizing the walls by water. The resistivity of the electrolyte then turns out to be at least an order of magnitude lower than the bulk solution outside the crack. The proposed solution to this dilemma is to assume that a considerable portion of the anodic current shown in Fig. 3 can be attributed to formation of soluble titanium species in parallel with oxide growth.

One point of view is that the difference between the experimental current density and the high-field conduction solution in Fig. 3 is current density for soluble titanium species. The electrolyte in the crack would then be less acid and have a resistivity closer to that of the bulk solution. Experiments are underway to evaluate the amount of parallel formation of soluble titanium species. Parallel formation of soluble species has been reported in the case of iron (17), zinc (18), and aluminum (19).

The zero-current intercept of the current versus potential plot in Fig. 4 occurs at a potential of about -800 mv. This coincides with the mixed potential experimentally found for oxidation of titanium and hydrogen ion reduction in an acid solution (13). Because of the high current densities ($\sim 1 \text{ amp/cm}^2$) for these reactions on newly generated metal surface, it is assumed that this mixed potential is established in the monolayer zone in a crack.

At applied potentials more positive or anodic to the mixed potential there would be a net generation of hydrogen ions in the crack and the electrolyte in the crack would tend to become acid. At applied potentials more negative or cathodic to the mixed potential there would be a net consumption of hydrogen ions and the electrolyte in the crack would tend to become alkaline. Cathodic protection for SCC at potentials more negative than the mixed protective is presumed to occur when the ratio of hydroxyl to halide ions in the crack reaches the level for inhibition.

Although some hydrogen ion reduction occurs in the monolayer zone in a crack, the amount is relatively small, on the order of a monolayer according to calculations of the mass-transport-kinetic model (14).

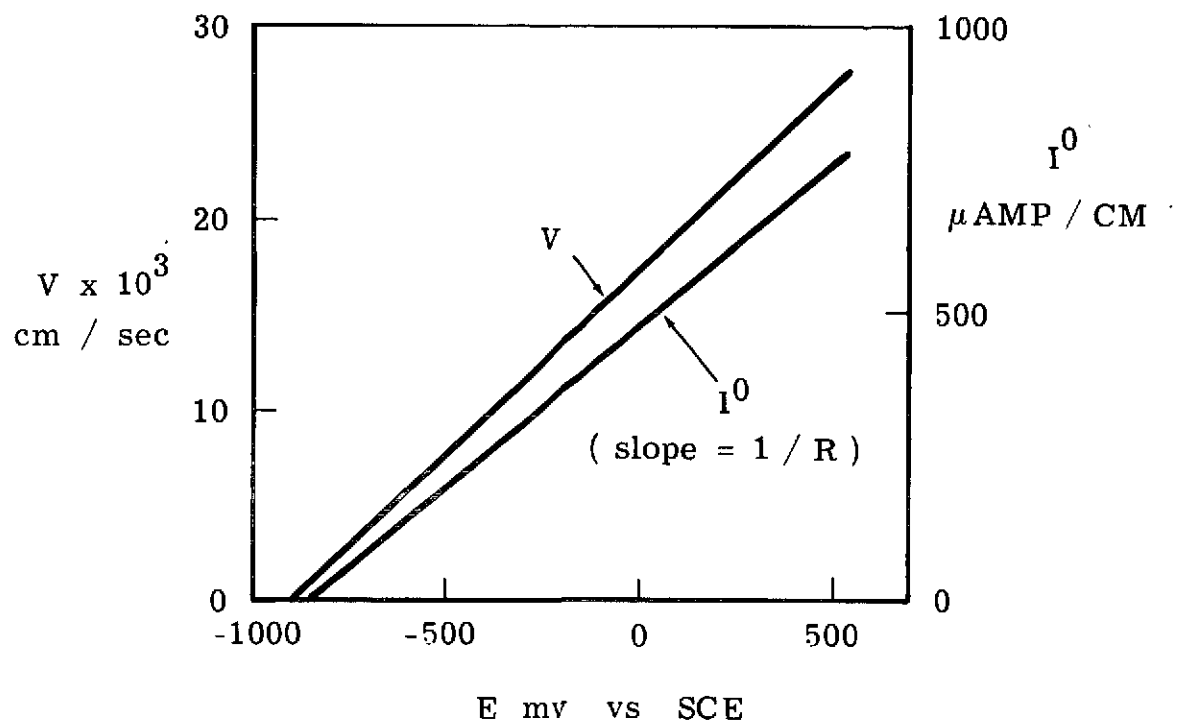


Fig. 4 Typical Relation of Velocity and Initial SCC Current to Potential in 0.6M Halide Solutions

A hydride mechanism of SCC propagation therefore appears improbable. The amount of oxide formed on the walls can also be shown to be too small for either the oxide cracking mechanism or the oxide wedging mechanism for titanium in aqueous solutions. In other words, the crack velocity is so high that the crack tip "outruns" the hydride and oxide.

5.0 FUTURE WORK

The following items of work are planned for the immediate future:

1. Investigate susceptibility of the Ti:8Mn alloy over a wider range of temperatures in the $\alpha+\beta$ phase field.
2. Investigate the influence of β -grain size on susceptibility.
3. Evaluate the stress criterion for fracture - on notched and un-notched specimens.
4. Investigate the influence of hydrogen charging on SCC.
5. Establish the fracture plane for SCC in Ti:8Mn alloy.
6. Resolve the problem of chloride analysis of titanium.
7. Refine and extend electrochemical kinetic studies to a wider range of halide concentrations and potentials and to other alloys.
8. Conduct experiments to determine quantitatively the amount of soluble titanium ion formed in parallel with oxide.
9. Include parallel soluble titanium ion formation in mass-transport-kinetic model.
10. Focus attention conceptually and experimentally on events at the crack tip.

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